Component Research for Redox Flow Batteries and 'Open' Batteries

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Thanks to: Imre Gyuk (OE OEDR)

Goals and Tasks

1. Demonstrate improved performance of RFBs in pre-competitive work
   – Chemistry agnostic; we look at *key representative processes*--- VRBs + New directions for higher ED (FY17)
2. Develop rational diagnostics to guide component selection
   – This year: focus on understanding differences in electrode behavior
3. New ‘Open’ Battery Directions for Higher Energy Density
   – Non-aqueous system
   – Metal/air
4. Begin some work on durability issues with PNNL

Approach

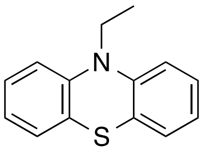
Working at Component, Cell Level to Extend Lessons Learned

Focus on what limits performance of an RFB

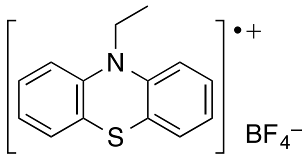
1. Membranes
   a. Continued testing of high performance membranes for VRBs
   b. Work on membranes for other chemistry
2. Electrodes
   a. Effect of electrode structure on performance
3. Broadened scope to other types of open battery systems (Metal/air, Non-aqueous)

High Performance in Non-aqueous System

N-ethylphenothiazine (EPT) acetonitrile electrolyte

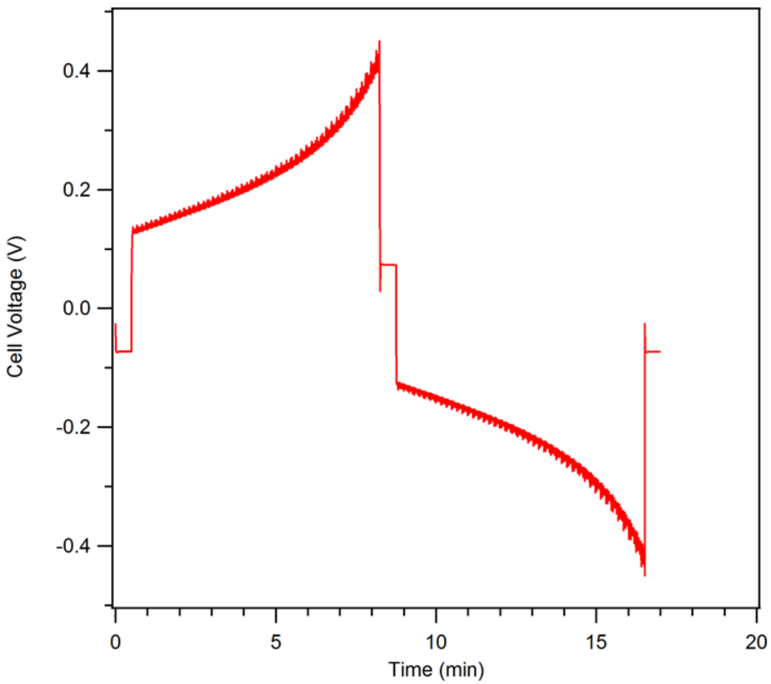


EPT

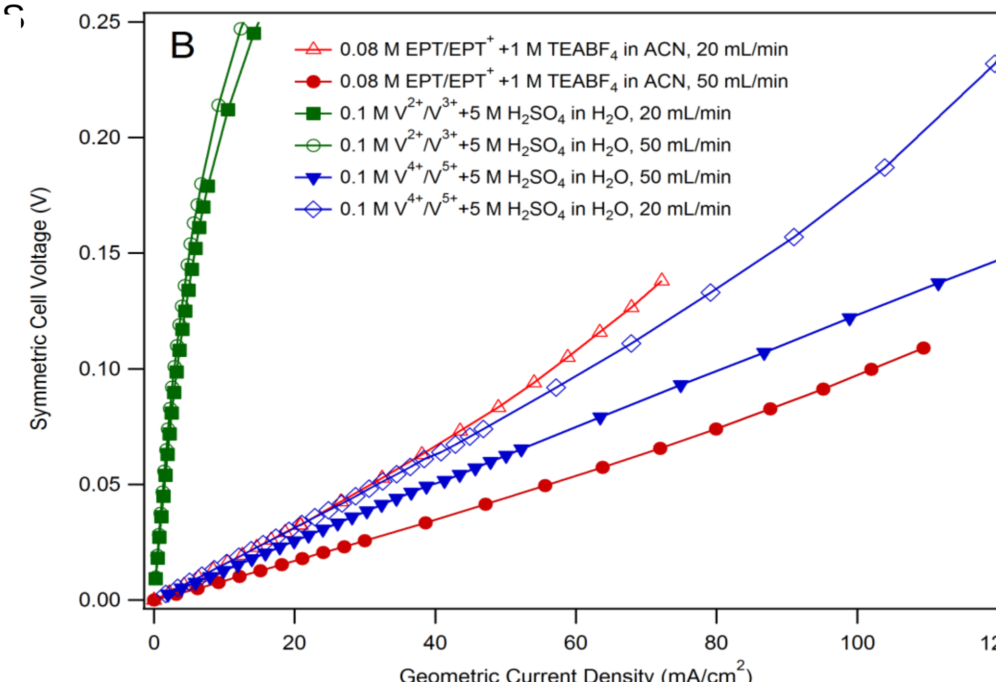


EPT-BF$_4$

Nonaqueous redox flow battery with 0.08 M EPT in catholyte and 0.08 M $EPTBF_4$ in anolyte with 1 M $LiBF_4$ in ACN supporting electrolyte operated as a symmetric cell to investigate the reaction kinetics and mass transport in S



The first cycle of symmetric battery cycling. Good cyclability illustrates the potential of stabilized cation radical in nonaqueous redox flow battery application.

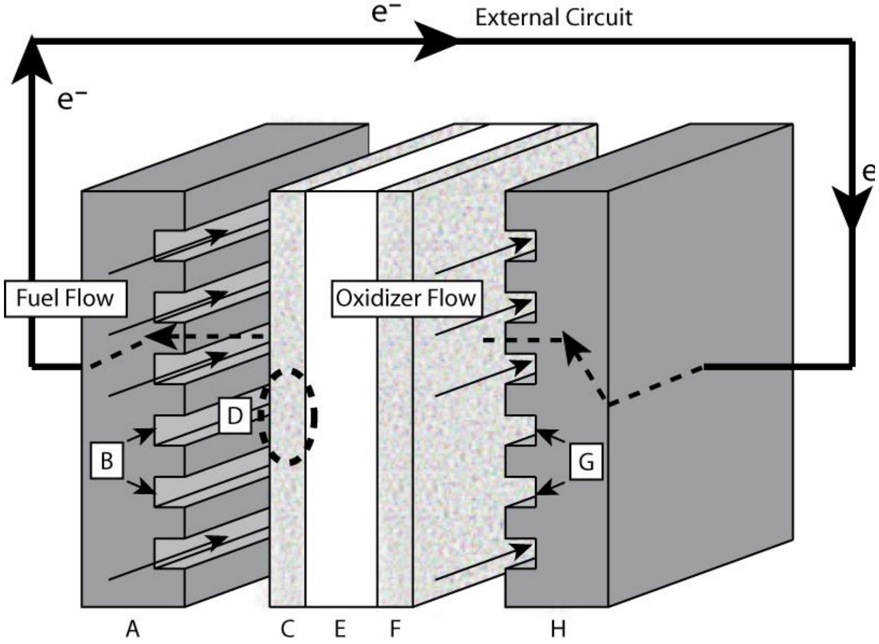


IR corrected Polarization curve of EPT/EPT+ in ACN on SGL carbon felt, in comparison to vanadium redox couples in aqueous electrolyte.

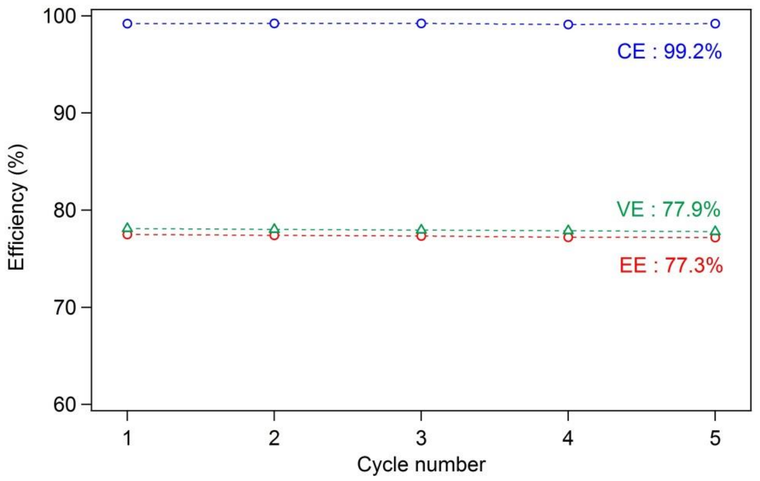
Managing Mass Transport in Cell

Transport at Flow Field/Electrode Interface is Critical Factor; Controlled by Electrode Morphology, Wetting

Flow-by Configuration



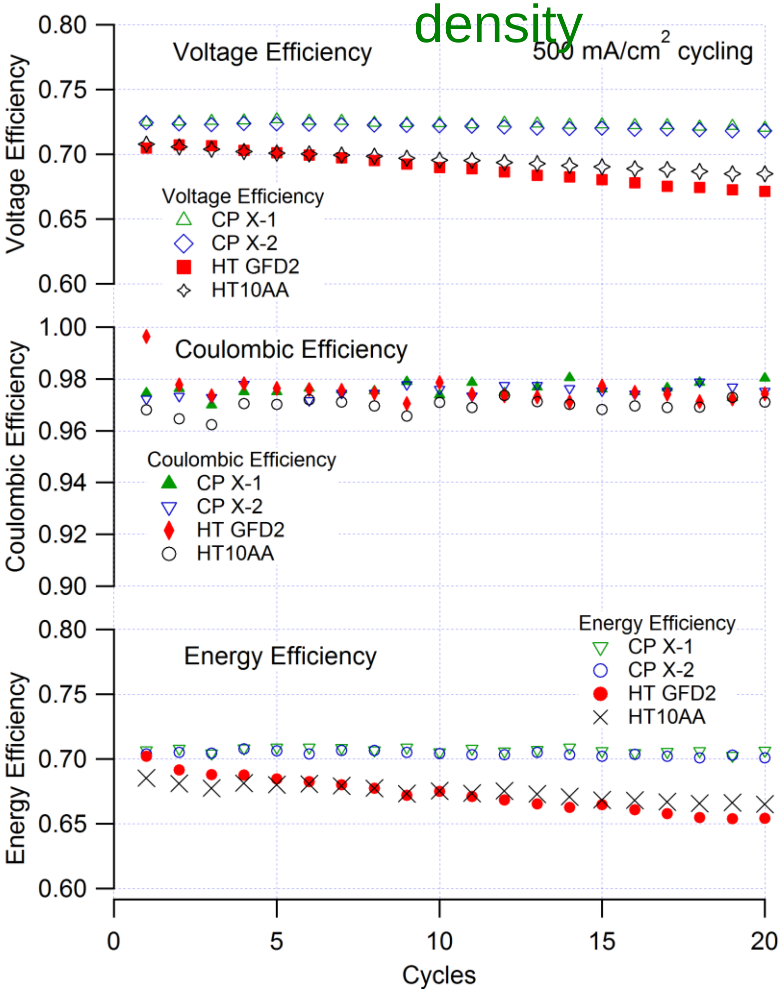
Cell Efficiency @ 500 mA/cm^2

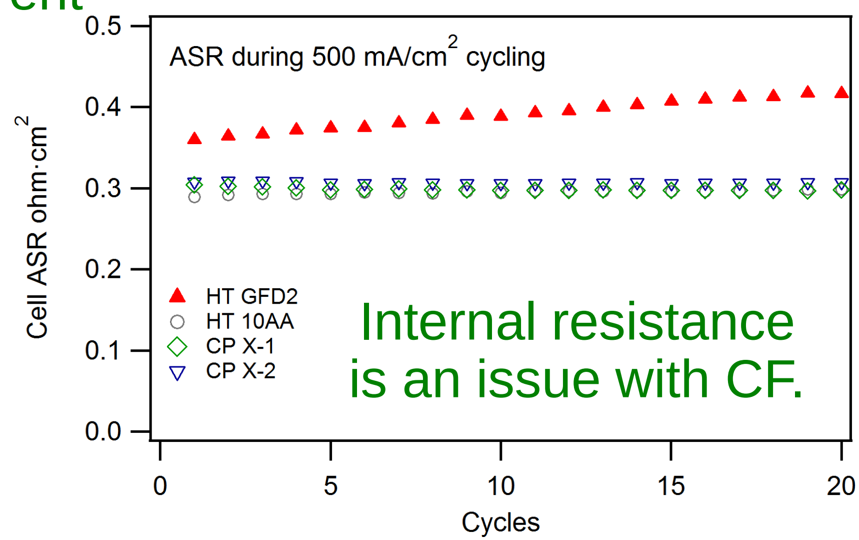


Now cycling between 20% and 80% SoC

Carbon felt: low cost alternative to achieve high current density in VRFB

Thermally activated carbon felt (SGL GFD2 EA) can perform well at high current density

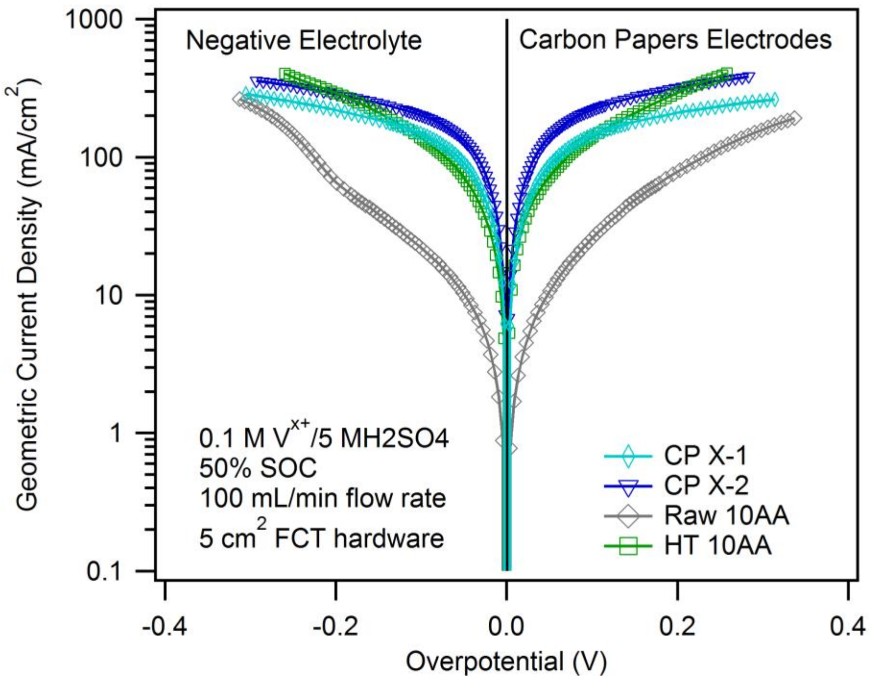


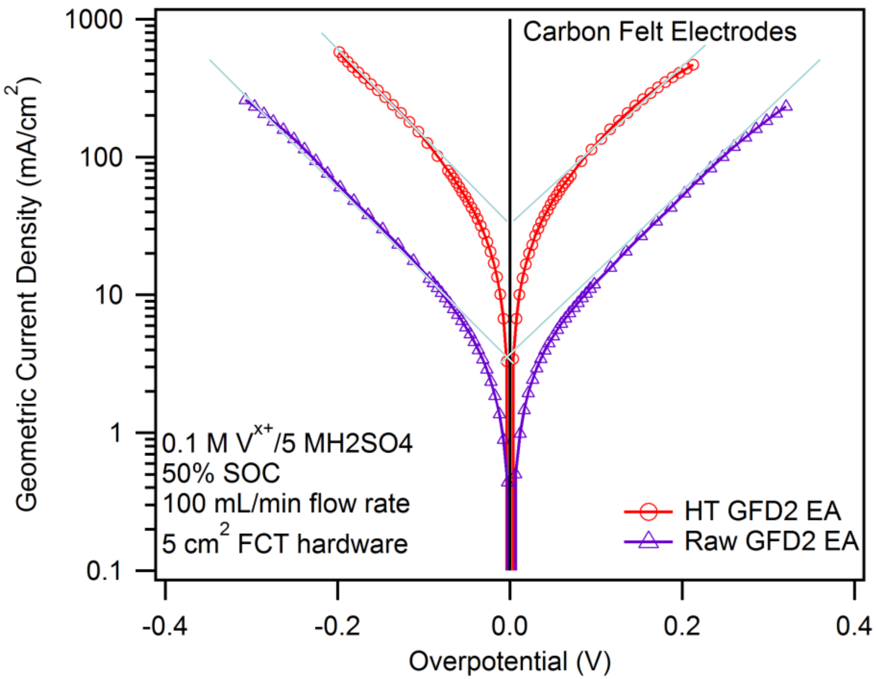


- **Current density 500 mA/cm^2, between 1.75V 1V;**
- Untreated Nafion 212; 30°C;
- 1.7 M V^{x+}/5 M Sulfate;
- 50 mL/min electrolyte flow rate;
- Carbon paper, 400 um-> 250 um;
- Carbon felt, 2.5 mm-> 1.25 um;
- Biologic VMP-80 booster;

Carbon Paper is advantageous in kinetic region, while carbon felt can facilitate mass transport

Polarization curve with symmetric cell collected with 0.1 M $V^{2/3+}$ in 5M sulfuric acid at constant 50% state of charge.

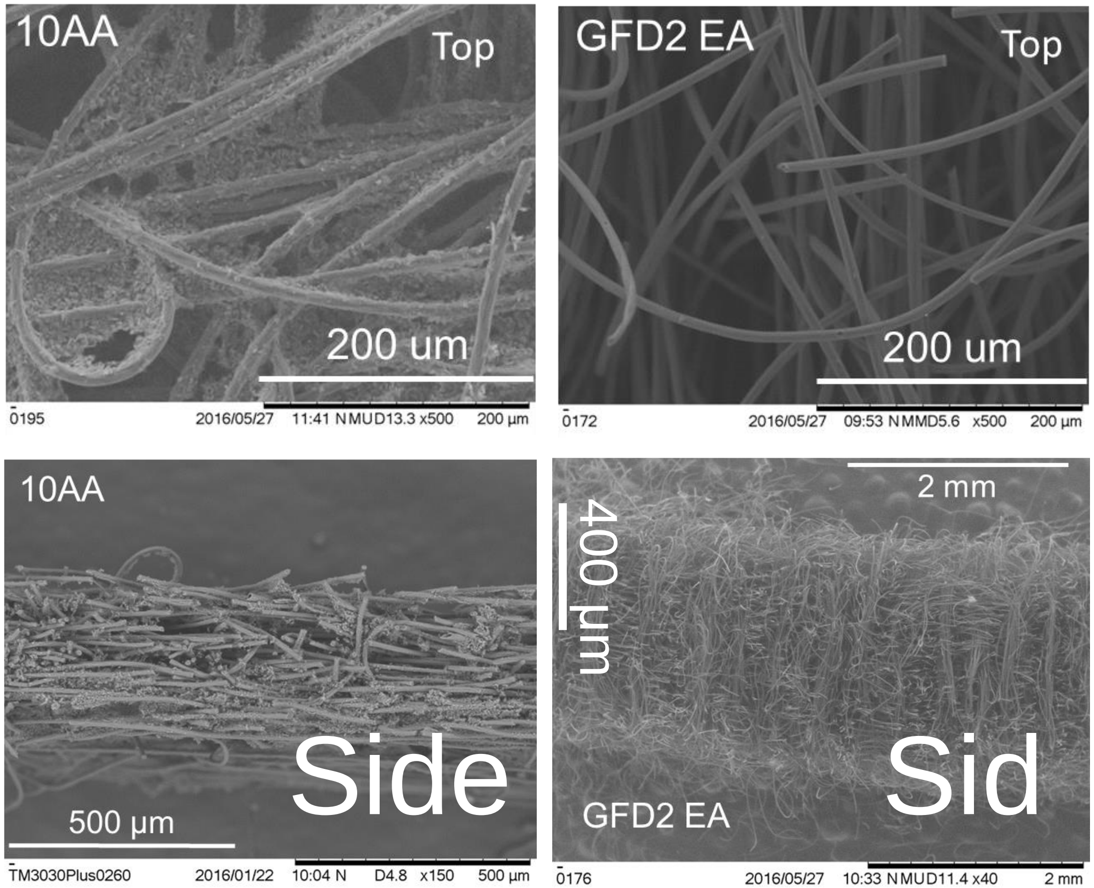




Carbon papers:
1. low activation loss due to high surface area;
2. High mass transport loss: abnormally high Tafel slope, ~1000 mV/decade; limited mass transport current density.

Carbon felts:
1. high activation loss due to low surface area;
2. Relatively low mass transport loss: normal Tafel slope, ~160 mV/decade; higher MT limiting current density.

Electrode engineering: to address over-potential associated with kinetics, mass transport and contact resistance



<u>Challenge of MT in liquid</u>

Ionic diffusivity in solution: ~10^{-5} cm^2/s;
Gas diffusivity: ~10^{-1} cm^2/s;

<u>Desired Component Features</u>

Kinetics: high surface activity to reaction, , high surface area, A;

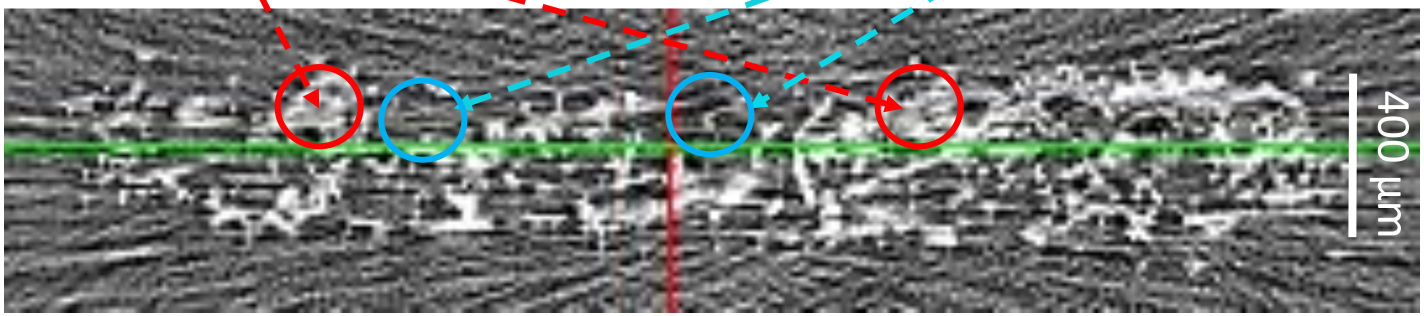
Mass transport: high MS limiting current densities: and
.

Surface area is enclosed in carbon paper, distant from open region where convective flow can occur

X-ray tomography as a new technique to analyze structure features in RFB electrodes

Carbon fiber and binder agglomerate, where surface area at.

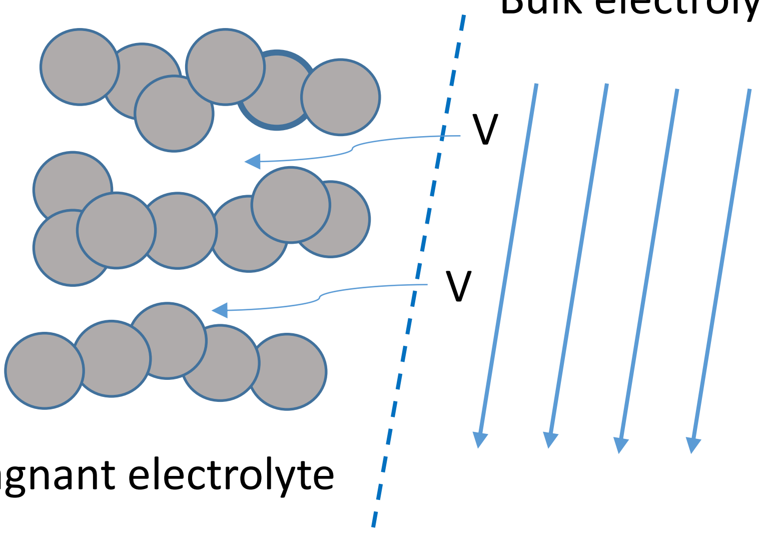
Open space for electrolyte flow



SGL 10AA carbon paper

Carbon agglomerate

Bulk electrolyte flow

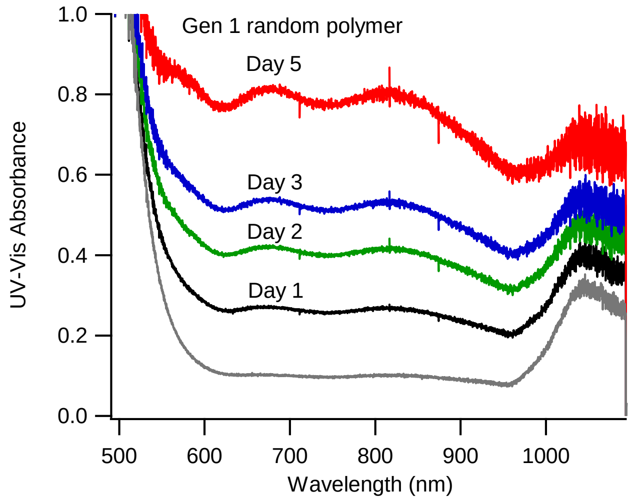


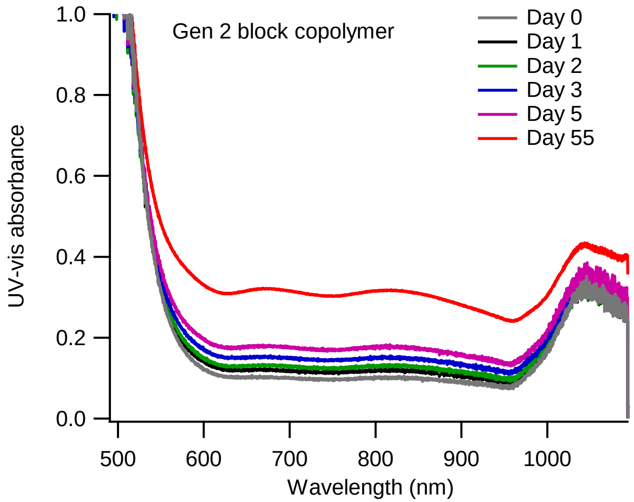
Stagnant electrolyte

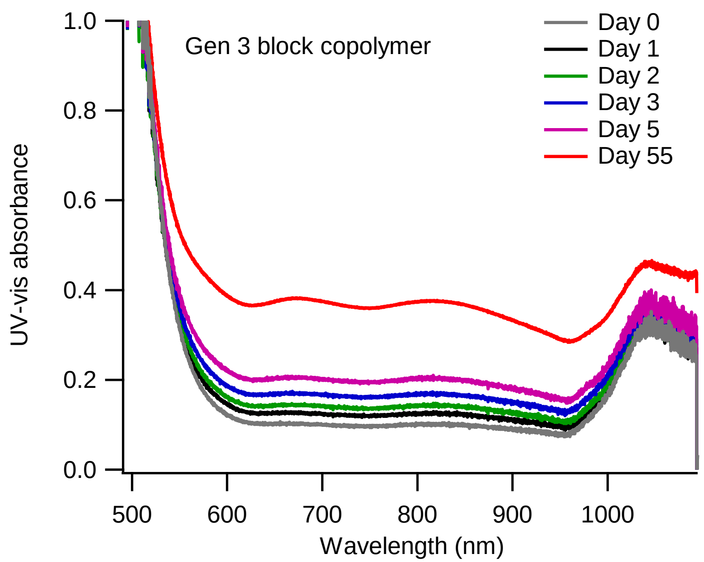
Feature sizing of carbon agglomerate in CP: 10~100 um;
Ion diffusivity in solution: ~10^{-5} cm^2/s.

Method under development in collaboration with Imperial College, UK

Durability Test: Improved Polymer Oxidative Stability Block copolymer SDAPP ion exchange membrane (SNL)







Membrane samples soaked in 1.7 M V^{5+}/5 M SO_4^{2-}; 22° C;

V^{4+} accumulation due to polymer oxidized by V^{5+};

Aliquot (Sampled) UV-Vis spectroscopic measurement;

Work is still on going; to combine chemical analysis to clarify degradation mechanism for future material development.

Summary

- High performance in NA system achieved
- Need to further characterize and understand electrode performance; Improve electrode/flow field interface
- Broadening membrane studies to include other chemistry
- Durability work barely beginning; some initial progress on membranes but electrode study also started

PROGRAMMATICS

Component Research for Redox Flow Batteries and 'Open' Batteries

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Objectives: Improve Performance of Open/Flow Batteries Through Component Optimization

FY16 Accomplishments

1. New membrane studies w/SNL
2. Studies of transport in carbon electrodes
3. Translating VRB research to WattJoule
4. New Directions based on studying key components
   – 'High' performance Nonaqueous RFBs
5. Initiated joint efforts with PNNL
6. 7 papers submitted/published in FY16

FY17 Goals

1. Continue component studies to improve membranes and electrodes

   Need radical improvements in membranes for new chemistries;

   Exploring paths to high energy density

2. Developing new diagnostics for transport, failure modes and durability
3. Strengthen and grow interactions
   – Continue to disseminate findings to industry

ORNL Research Plan for RFBs Interactions

Continue to interact with component manufacturers

- Extend discussions beyond VRB
- Multiple sources of electrode materials
- New analysis approaches through ICL collaboration

Collaborations with SNL, PNNL, membrane, electrode makers

- Cy Fujimoto: feedback from our testing driving synthesis
- PNNL: beginning effort tied to durability/reliability
- Leverage from industry-funded collaborations at UTK and ORNL

Next Steps

1. Continue component studies to help identify key chemistry and structure aspects for improved membranes and electrodes
   - Improve cycling capabilities
   - Extend study of components for non-VRB, aqueous chemistries
2. Developing new diagnostics for failure modes and durability, exploiting available work plus new techniques
3. Moving on to promising chemistries beyond VRB
4. Strengthen and grow interactions
   - Good start this year with PNNL

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1. Thanks to Imre Gyuk and OE
2. Thanks to my team at ORNL and UTK and the Bredesen Center.
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5. Thanks to Nigel Brandon and his team at Imperial College, Vito DiNoto in Padua and others with whom I was able to work with and discuss 'open batteries' during my European sojourn.